Low Temperature Synthesis of Some Ternary Transition Metal Sulfides in Fxcess Sulfur and Their Characterization(過剰イオウ共存下における三元系遷移金属複硫化物の低温合成とキャラクタリゼーション)

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論文内容要旨

Metal sulfides are expected to and actually often show similar physico-chemical properties to the corresponding oxides on account of the position of sulfur in the periodic table immediately below oxygen. A large number of metal oxides and mixed metal oxides have been prepared, some of which are known to be industrially used as materials for devices utilizing their excellent electrical, magnetic, optical, mechanical or chemical properties. In contrast to the oxides, the study of metal sulfides and mixed metal sulfides is sparse due to difficulty in preparing these compounds though the properties of sulfides, whose bonding nature is usually more covalent than oxides, are assumed to be promising. In this work, two synthetic methods to form mixed metal sulfides at low temperatures were developed. Such methods are attractive to prepare the mixed metal sulfides which have good properties but are unstable and decompose at higher temperatures. In any cases, the addition of halides was found to be effective for having high yields of the mixed sulfides. For the obtained mixed sulfides, X-ray diffraction analyses were carried out. The crystal structure of $NdCuS_2$ was closely examined by means of the Rietveld method. The results obtained in this work are summarized as follows.

Chapter 1　Introduction

In this chapter, the background of sulfide research was first overviewed. Although the physico-chemical properties of sulfides are alike to oxides, there are still significant differences which are caused by large polarizability of sulfur anions, sulfur-sulfur bonding and participation of anion 3d orbitals in bonding which leads to stabilization of trigonal prismatic coordination of sulfur anions. Explanation is given for important structure types of the transition metal sulfides. They are monosulfides, disulfides, trisulfides and related poly-sulfides, metal rich sulfides and ternary transition metal sulfides $A_xM_yS_z$ which can be classified into three categories according to the type of the A-S and M-S bonds where M are the metals (usually transition metals) having a higher oxidation state than A metals.

The synthetic methods for transition metal sulfides were then reviewed. The sulfides have been prepared by the ceramic methods, the gaseous sulfurization methods, and the chemical vapor transition methods. However, such methods all require the reaction at high temperatures. There have been low temperature methods for the preparation of sulfides, but they are limited to electrochemical intercalation or topochemical ion-exchange of alkali metals or alkaline earth metals to peculiar sulfides. The development of more general low temperature method for preparation should make it possible to prepare the metal sulfides and mixed metal sulfides which are unstable at higher temperatures.

In this work, two low temperature methods for the synthesis of ternary transition metal sulfides have been proposed and experimented. (1) The first method comprises heating of the component metals or metal sulfides in large amounts of sulfur melt. The sulfur melt plays a role of solvent of the component sulfides as well as reactant. The syntheses are made in a sealed evacuated Pyrex ampoule at temperatures between 573-723 K. Ba_xTiS_y and $PbTiS_3$ were exemplified to be successfully synthesized by this method. (2) In the case of the second method, the component sulfides are heated together with rather smaller amounts of sulfur in sealed ampoules at somewhat higher temperatures of 723-873 K. By this modified method, a less reactive ternary sulfide of $BaZrS_3$ was formed with a high yield. The present study was extended to the analysis and characterization of the mixed transition metal sulfides obtained by the low temperature methods, which include the crystal structure determination of $NdCuS_2$ by the Rietveld method.

Chapter 2 Computer programs for the calculation and refinement of crystal structures

A brief explanation about the computer programs used in this work for X-ray diffraction crystal analysis is made. The CELL programs were used for finding possible space groups and lattice parameters from the first twenty observed diffraction lines. The LCR2 program allowed to calculate the lattice parameters of the known crystal system by nonlinear least squares refinement from the X-ray powder diffraction data employing several correction functions including the Nelson-Riley extrapolation function. The LAZY-PULVERIX program calculates the theoretical X-ray peak positions and intensities. The first routine LAZY reads the data and prepares the input for the second routine PULVERIX, which is the main routine for calculating powder diffraction patterns. The RIETAN program consists of two separated programs coded in FORTRAN in which the first program is for this work of angle-dispersive X-ray diffraction analysis. This program calculates the refined crystal parameters. The ATOMS program was used to visualize the atom arrangements for the fixed crystal structures, which draws e.g. spherical atoms and stick or bond type, line bonds only, interpenetrating spherical atoms and coordination polyhedra.

Chapter 3 Experimental

Both the two methods of synthesis were carried out by heating the starting materials mixtures of total weights ranging from 1.8 to 2.0 g in evacuated sealed Pyrex or quartz ampoules. From the reacted mixtures, sulfur was separated first by filtration of sulfur melt followed by dissolution of the remaining sulfur into CS_2. The filtration was implemented using a separation system designed for this purpose which is composed of two parts; a vertical resistance tube-furnace, and a Pyrex glass separator connected to evacuation line. The ampoule with one end cut opened was set in the separator with its open-end downward on the glass filter, and then the separator was heated in the furnace during suction by a rotary pump. The water soluble impurities such as BaS_3 and $BaCl_2$ were removed by water treatment followed by acetone-drying. The X-ray powder diffractometry was performed with a Rigaku RAD-IC diffractometer using Cu$K\alpha$ radiation (40 kV, 20 mA) monochromatized by curved pyrolytic graphite. The metals in the product were determined by inductively

coupled plasma emission spectroscopy (ICP-ES) using a PERKIN ELMER Optima 3300 XL spectrometer. Hydrochloric acid of 4 or 6 M was used for dissolving the sample as well as diluting the standard solutions.

Chapter 4 Synthesis of Ba_xTiS_y in sulfur melt

The low temperature synthesis in large excess of sulfur was studied for the reactions of (1) $BaS + TiS_2$+ 50 S (melt) and (2) 0.9 BaS + 0.1 $BaCl_2$ + TiS_2 + 50 S (melt) to form Ba_xTiS_y. The starting materials were sealed in evacuated Pyrex ampoules and heated at temperatures 623-723 K for 1-3 weeks. After the separation of sulfur, the products were Ba_xTiS_y, BaS_3 and TiO_2 (and $BaCl_2$ in the case of reaction (2)). The object mixed sulfide, Ba_xTiS_y, was formed with the yields around 0.80 (mole fraction), and no significant change of this value with temperature between 623 and 723 K was observed for reaction (1). Meanwhile for reaction (2), the Ba_xTiS_y yield was 0.80 at 623 K, but it increased to 0.89 at 723 K. Sixty percent of added $BaCl_2$ was estimated to be removed in sulfur when its melt was separated. Chemical analysis for x and y values in Ba_xTiS_y showed that the x value slightly increased with heating temperature whereas both the x and y values did not change with heating time. The y value for reaction (1) decreased from 3.8 at 623 K to 3.0 at 723 K. The y values for reaction (2) were in the vicinity of 3.0 at all temperatures studied.

Chapter 5 Synthesis of $PbTiS_3$ in sulfur melt

The formation of $PbTiS_3$ was studied for fourteen combinations of starting materials at temperatures ranging from 573 to 723 K. As the sources of lead, Pb metal powder, PbS, $PbCl_2$ and PbI_2 were used. One (or two) of these and TiS_2 were mixed with sulfur having a mole ratio 50 times as large as TiS_2. The ratio of the integrated intensity of the strongest X-ray diffraction peaks of $PbTiS_3$ and PbS was ascertained to be proportional to the ratio of the mole fractions of these compounds. If 10 mole % $PbCl_2$ was added, the mole fraction of $PbTiS_3$ formed was already 0.53-0.63 at 573 K, and it increased to 0.86 at 598 K. However, without $PbCl_2$, the $PbTiS_3$ yield was only 0-0.13 at 573 K, though it increased with increasing temperature. The effect of heating time was not large in 2-10 days of heating in the present experiment. $PbTiS_3$ was obtained in almost a single phase if the PbS amount in the starting materials was diminished to 0.5-0.6. The decrease of the addition amount of $PbCl_2$ to 0.05 caused a decrease in the $PbTiS_3$ yield.

Chapter 6 Effect of halide addition on the syntheses of $PbTiS_3$ and Ba_xTiS_y in sulfur melt

In this chapter, the effect of the halides MX_2 (M=Ba and Pb) was investigated more closely than in Chapters 4 and 5 using X= F, Cl and I by changing the reaction conditions. The formation of $PbTiS_3$ was studied for the reactions of Pb metal powder and TiS_2 in 50 S melt with and without the addition of PbF_2, $PbCl_2$ or PbI_2. The effect of PbX_2 is large at 623 K for all halides, although there is a distinct difference in the yield of $PbTiS_3$ in the three halides, i.e. the largest yield of 0.74 was obtained by $PbCl_2$ and the smallest yield of 0.44 by PbF_2. Because the yield of $PbTiS_3$ without the addition of PbX_2 was 0.24, its increase is as large as 0.50 for $PbCl_2$. However, when the heating temperature was raised to 673 K, the yield without PbX_2 increased up to 0.59 approaching the yields obtained with PbX_2.

Next, the formation of Ba_xTiS_y was studied for the reaction of BaS and TiS_2 in 50 S melt with and without the addition of BaF_2, $BaCl_2$ or BaI_2. In contrast to the $PbTiS_3$ case, the yield of Ba_xTiS_y decreased with increasing temperature due to the formation of BaS_3. Namely, the large effect of $BaCl_2$ and BaI_2 on lifting the Ba_xTiS_y yield is in suppression of BaS_3 formation. The highest yield of 0.96 was obtained at 723 K with the addition of 10 mole % BaI_2. One important factor of such effects was considered to be in decreasing the sulfur vapor pressure in the ampoules. Some other possible factors were discussed.

Chapter 7 Synthesis of $BaZrS_3$ in the presence of excess sulfur

For the reactions adopted in the former chapters in large amount of sulfur melt, the heating temperature cannot be raised above 723 K because of the increase of sulfur vapor pressure in the ampoules. However, for $BaZrS_3$ synthesis, higher temperatures than 723 K were required. To meet this condition, the reaction in a small excess amount of sulfur was studied. It was found that $BaZrS_3$ could be synthesized with high yields by heating at temperatures of 723-873 K, if a proper amount of sulfur (the addition ratio of sulfur, α, is between 0.5-1.5) and 10 mole % of $BaCl_2$ were added and mixed in the starting materials. $BaZrS_3$ could be formed in a short period of 10 min, and the highest yield of 0.96 was obtained after 1 h heating for the sample of $\alpha = 2.0$. At 773 K, the reaction was slower, and the highest yield of 0.87 was obtained after 3 h for the sample of $\alpha =$ 1.5. At least 12 h of heating time was necessary for the reaction at the lower temperature of 723 K. The highest yield of 0.77 was obtained after 7 days for the sample of $\alpha = 1.0$. The addition of sulfur is thought to give a necessary sulfur pressure for the formation of $BaZrS_3$. The addition of 10 mole % BaX_2, especially $BaCl_2$ was essential to have $BaZrS_3$ with high yield.

Chapter 8 Synthesis and the crystal structure analysis of $NdCuS_2$

Ternary sulfide, $NdCuS_2$, was synthesized with high yield by heating the binary sulfides of Nd_2S_3 and CuS either in a large amount of excess sulfur melt at 723 K or in the presence of a small amount of excess sulfur at 873 K if 10 mole % of $CuCl_2$ or CuCl was added and mixed in the starting materials. $NdCuS_2$ was also obtained by heating the mixture of Nd_2S_3 and CuS without the addition of sulfure in evacuated sealed ampoules if the heating temperature was as high as 1273 K. Since for this compound no crystal data other than the crystal system and lattice parameters had been reported, crystal structure analysis was performed by powder X-ray diffractometry using the Rietveld method. $NdCuS_2$ crystallized in monoclinic system, space group $P21/c$, and a=6.520, b=7.169, c=6.829 A and β=98.48° with Z=4. This crystal is isostructural with $LaCuS_2$, built up of sheets parallel to the b and c axes. One sheet is made of Nd_4S tetrahedra and has the composition NdS; the other is formed by CuS_4 tetrahedra arranged in pairs which alternate with pairs of empty tetrahedra.

Chapter 9 Conclusion

Two low temperature methods for the synthesis of ternary transition metal sulfides in sealed evacuated ampoules have been studied. Ba_xTiS_y and $PbTiS_3$ were successfully synthesized by method (1). Ba_xTiS_y was formed with the yields of 0.80-0.89 by the reaction of BaS and TiS_2 in 50 S at 623-723 K. The addition of 10 mole % $BaCl_2$ was effective to increase the yield at lower temperatures. For the synthesis of $PbTiS_3$, the mixture of PbS(or Pb) and TiS_2 were heated together with 50 S at 573-723 K. If 10 mole % $PbCl_2$ was added, the yield of $PbTiS_3$ increased to 0.86 at 598 K. The effect of halide addition was studied. It was shown that marked enhancement in the yields was attained by the addition of chlorides and iodides especially at lower temperatures. This mechanism was discussed. $BaZrS_3$ was synthesized by method (2) at 723-873 K. The highest yield of 0.96 was obtained from the combination of starting materials $0.9\,BaS + 0.1\,BaCl_2 + ZrS_2 + 2\,S$ during 1 h heating at 823 K. $NdCuS_2$ was found to be synthesized by either of the methods. The crystal structure of this compound was closely analyzed by X-ray diffractometry using the Rietveld method.

The low temperature method studied and developed in this study gives mixed metal sulfides with high yields. The method would become of essential importance for the synthesis of the mixed metal sulfides which have excellent and useful physico-chemical properties but are unstable at higher temperatures adoped by the ordinary synthetic methods of mixed metal sulfides.

審査結果の要旨

硫化物は酸化物との関連において興味が持たれており，優れた物性を示す酸化物，複酸化物に対応して，いろいろな硫化物，複硫化物が知られている．硫化物は酸化物よりも一般に共有結合性が強く，それに伴う新物性の発現も期待される．しかし，硫化物の研究は少なく，その大きな原因として硫化物の合成の難しさが指摘されている．そこで，硫化物合成の手法を広げ，容易な合成を可能にする研究が要望される．

本論文は，このような観点から，三元系遷移金属複硫化物について，通常の高温合成法では分解し，合成できないような低温安定相の合成も可能とするような低温合成法を研究した．本法による高収率での合成を実証するとともに，得られた複硫化物の構造を粉末 X 線回折法により詳しく解析したもので，全編９章より成る．

第１章は序論であり，本研究の背景および目的を述べている．

第２章では本研究で生成物の定量に用い，また結晶構造解析に用いた計算プログラムについて述べた．CELL，LCR2，LAZY-PULVERIX，RIETAN，ATOMS プログラムについて記した．

第３章では本研究に共通した実験方法と手順について述べている．低温合成法１は 50 当量の大過剰イオウ共存下で成分硫化物を真空封管中で加熱，反応させる．溶融イオウは反応物質であるとともに，溶媒の役割も果たす．低温合成法２は反応温度が高い場合に適する．イオウ混和量を２当量までに制限し，イオウ蒸気圧を下げて反応させる．過剰イオウは高温吸引ろ過により反応生成物より除去する．

第４章は低温合成法１による Ba_xTiS_y の合成実験の結果を記している．BaS と TiS_2 に 50 倍のイオウを加え，623-723 K で反応させた．反応助剤として $BaCl_2$ を添加すると収率が向上し，723 K で 0.89 に達した．

第５章は低温合成法１による $PbTiS_3$ の合成結果を述べた．PbS と TiS_2 の反応に 50 倍のイオウと $PbCl_2$ あるいは PbI_2 を添加した影響を調べた．温度が高いと $PbTiS_3$ の収率が高まり，598 K で 0.86 を得た．

第６章では Ba_xTiS_y と $PbTiS_3$ の合成に際してのハロゲン化物添加の影響を調べた．Ba_xTiS_y の生成量は 10 モル%の BaI_2 を加えたとき最大で，723 K で 0.96 に達した．フッ化物，塩化物，ヨウ化物などハロゲン化物の影響は，温度が低い場合に大きくなることが分った．

第７章では低温合成法２による $BaZrS_3$ の合成について調べた． $BaCl_2$ 添加，723 K の反応条件下で，BaS と ZrS_2 の反応により 10 分間で $BaZrS_3$ 生成反応が始まり，１時間後には 0.96 の収率が得られた．

第８章では低温合成法１，２で $NdCuS_2$ を合成し，生成物について Rietveld 法を用いて詳細な粉末 X 線解析を行い，結晶構造を定めた．構造パラメーターを求め，類似の他種化合物と比較・検討を行った．

第９章は結論である．

以上要するに本論文は，三元系遷移金属複硫化物の合成法に関し，高温では不安定な硫化物の合成を可能とする低温合成法を考案し，Ba_xTiS_y，$PbTiS_3$，$BaZrS_3$ および $NdCuS_2$ を合成して本法を実証するとともに最適反応条件を検討し，キャラクタリゼーションを行い，特に $NdCuS_2$ については合成ののち詳しく結晶構造を定め，精密化を行ったものである．本研究の主眼とする新合成法は硫化物研究に役立つ有力な手法を提供するもので，量子エネルギー工学，無機合成工学の発展に寄与するところが少なくない．

よって，本論文は博士(工学) の学位論文として合格と認める．